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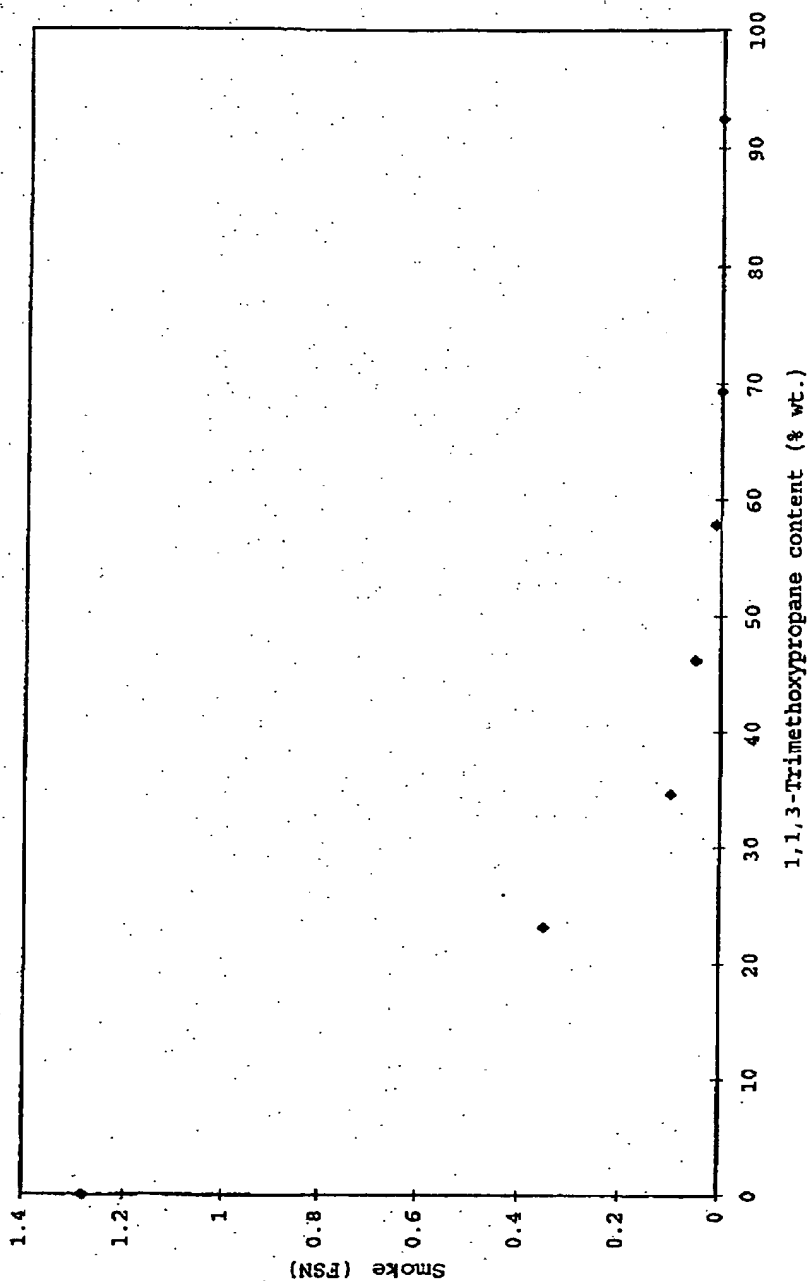
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(54) Abstract Title
Fuel compositions with reduced soot emissions

(57) A fuel composition for a compression-ignition engine comprising one or more trialkoxyalkanes, wherein said one or more trialkoxyalkanes are present in an amount in the range of from 50 to 100 % wt. based on said fuel composition; a method of operating a compression-ignition engine, which comprises introducing into the combustion chambers of said engine said fuel composition; and the use in a compression-ignition engine of said fuel composition to reduce soot emissions. Preferred additives are 1,1,3-trimethoxypropane and 1,1,3-triethoxypropane.

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FUEL COMPOSITIONS

The present invention relates to fuel compositions, preferably diesel fuel compositions, their use in compression-ignition engines, and methods of operating said engines.

5 Although diesel engines are highly efficient, they are unsatisfactory in terms of emissions, especially of particulate matter.

10 Particulate matter is a result of the pyrolysis and partial oxidation of fuel during combustion. Particulate matter consists of soot, unburnt or partially burnt fuel condensed on soot particles (also known as the soluble organic fraction), and sulphuric acid. The soluble organic fraction can be removed using an oxidation catalyst. The amount of sulphuric acid present in
15 particulate matter as a result of the combustion of low sulphur fuels in current engines is minimal.

Agglomeration of soot particles present leads to smoke.

The effect of particulate matter on health and the environment is of increasing concern. As a result,
20 regulatory authorities are placing increasing restrictions on the acceptable limits for emissions from diesel engines.

Diesel fuel emissions are subject to a trade-off between the level of NO_x emissions and the level of
25 particulate matter emissions in that measures taken to reduce NO_x emissions such as injection timing changes tend to increase particulate emissions and vice versa.

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Whilst the advance of engine design has lead to large reductions in emissions, breakthrough performance may require special, improved fuels.

Such fuels would offer premium emissions performance in conventional engines and outstanding performance in improved engines.

Thus, it is highly desirable to lower particulate emissions in diesel fuels to such an extent that it is possible to have zero soot emissions, and therefore zero smoke emissions.

Both the sulphur content and other fuel properties such as density and cetane number will have an effect on the amount of particulate matter.

It has been shown, for instance in "Improvement of diesel combustion and emissions with addition of various oxygenated agents to diesel fuels", Miyamoto et al., Soc. Automot. Eng., SP-1206 (Diesel Engine Combustion and Emission Control):193-199, 1996, that oxygen-containing diesel fuels can lead to significant reductions in smoke and particulate emissions.

WO-A-98/56879 concerns a fuel composition comprising a major part of at least one fuel base and a minor part of at least one oxygenated compound, characterised in that it contains at least 0.05 % by weight of at least one trialkoxyalkane. The use of said compounds in diesel fuels is said to increase the cetane number of the resulting diesel fuel composition. A number of trialkoxyalkanes including trimethoxypropane, triethoxypropane, tripropoxypropane, tributoxypropane, 1,1,3-trimethoxybutane, 1,1,3-triethoxybutane, 1,1,3-tripropoxybutane and 1,1,3-tributoxybutane are said to be suitable for this purpose. Tri(methoxyethoxy)propane, tri(ethoxyethoxy)propane, 2-(2-hydroxyethyl)ethoxy-1,3-dioxolane, 1,1,3-triethoxy-2-methylpropane, 1,3,3-

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triethoxybutane and 1,1,3-triethoxycyclohexane are also preferred compounds. However, of the large number of compounds mentioned, only one compound, 1,1,3-triethoxypropane, is specifically exemplified.

5 WO-A-98/56879 further mentions that the use of such compounds makes it possible to limit the amount of aromatic hydrocarbons and sulphur-containing compounds that are responsible for the emission of particles. However, this is not elaborated on any further.

10 Although particulate emissions in diesel fuels can be reduced by limiting the amount of aromatic hydrocarbons and sulphur-containing compounds present in said fuels, this approach is not ideal. Such a process is costly, and requires additional investment in specialised refinery
15 equipment. In addition, the improvements that are achievable by this method for changing the composition of hydrocarbon fuels are limited.

It is therefore highly desirable to find alternative methods for the reduction of particulate emissions from
20 diesel fuels that go beyond that achievable with hydrocarbon fuels.

It has now been surprisingly found that the use of trialkoxyalkanes as a major component in diesel fuels can reduce soot emissions to extremely low levels, and that
25 in certain proportions such compounds can actually reduce said emissions to zero.

According to the present invention there is provided a fuel composition for a compression-ignition engine comprising one or more trialkoxyalkanes, wherein said one
30 or more trialkoxyalkanes are present in an amount in the range of from 50 to 100 % wt. based on said fuel composition.

Said one or more trialkoxyalkanes are preferably present in an amount in the range of from 55 to 100 %

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wt., more preferably 57 to 100 % wt., most preferably 57 to 75 % wt., based on said fuel composition.

In another aspect, the present invention provides a method of operating a compression-ignition engine, which comprises introducing into the combustion chambers of said engine a fuel composition according to the present invention as defined above.

The present invention further relates to the use in a compression-ignition engine of said fuel composition of the present invention. Particularly, it relates to the use in a compression-ignition engine of such a fuel composition to reduce the levels of soot produced in said engine as compared to the levels of soot produced when the engine is operated using a fuel composition not comprising said one or more trialkoxyalkanes.

The single Figure of the accompanying drawing illustrates the level of smoke emissions from a diesel fuel composition comprising Swedish Class I diesel fuel, and varying proportions of 1,1,3-trimethoxypropane.

Middle distillate fuel oil can be derived from petroleum and typically has a boiling range in the range 100°C to 500°C, e.g. 150°C to 400°C. Such petroleum-derived fuel oil may comprise atmospheric distillate or vacuum distillate, or cracked gas oil or a blend in any proportion of straight run and thermally and/or catalytically cracked distillates. Fuel oil compositions of the present invention are diesel fuel compositions.

Diesel fuels typically have an initial distillation temperature of approximately 150°C to 210°C and a final distillation temperature of 290 to 390°C, depending on fuel grade and use.

The diesel fuel itself may be an additised (additive-containing) fuel or an unadditised (additive-free) fuel. If the diesel fuel is an additised fuel, it will contain

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5 minor amounts of one or more additives, for example, one or more additives selected from anti-static agents, pipeline drag reducers, flow improvers (for example, ethylene/vinyl acetate copolymers or acrylate/maleic anhydride copolymers) and wax anti-settling agents (for example, those commercially available under the trade marks "PARAFLOW" (for example, "PARAFLOW" 450; ex Infineum), "OCTEL" (for example, "OCTEL" W 5000; ex Octel) and "DODIFLOW" (for example, "DODIFLOW" v 3958; ex 10 Hoechst).

The present invention is not limited by the sulphur content, aromatic hydrocarbon content, density or viscosity of the diesel fuel composition.

15 Other desired properties for said diesel fuels are disclosed in the European CEN 590 specification.

The number of carbon atoms present in trialkoxyalkanes according to the present invention is not limited, but may conveniently be from 4 to 18, preferably from 5 to 12, and more preferably from 6 to 9.

20 Alkoxy substituents of trialkoxyalkanes according to the present invention may be identical or different, and may also be linear or branched. Said alkoxy substituents may contain from 1 to 5 carbon atoms, preferably from 1 to 3 carbon atoms. Said alkoxy substituents may contain 25 further heteroatoms, in particular more than one oxygen atom.

Two of the alkoxy substituents may be linked to form a heterocycle of 5 or 6 atoms.

30 The alkane may be linear, branched or cyclic, and may contain further substituents in addition to said alkoxy substituents.

The substitution pattern of the alkoxy substituents is not limited. Said alkoxy substituents may be each attached to different carbon atoms of the alkane.

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Alternatively, two of said alkoxy substituents may be attached to the same carbon atom of the alkane.

Alternatively, all three of said alkoxy substituents may be attached to the same carbon atom of the alkane, i.e. a terminal carbon atom of the alkane.

Substitution may occur at either mid-chain or terminal positions of the alkane.

Preferred trialkoxyalkanes according to the present invention include trimethoxypropane, triethoxypropane, tripropoxypropane, tributoxypropane, tri(methoxyethoxy)propane, tri(ethoxyethoxy)propane, 2-(2-hydroxyethyl)ethoxy-1,3-dioxolane, 1,1,3-trimethoxybutane, 1,1,3-triethoxybutane, 1,1,3-tripropoxybutane, 1,1,3-tributoxybutane, 1,1,3-triethoxy-2-methylpropane and 1,3,3-triethoxybutane, 1,1,3-triethoxycyclohexane. Particularly preferred compounds are 1,1,3-trimethoxypropane and 1,1,3-triethoxypropane.

It is particularly preferred that the one or more trialkoxyalkanes are present in an amount sufficient to reduce smoke emissions of the fuel composition to zero upon combustion.

The present invention will now be illustrated by way of example by the following Examples.

In the following description, all parts and percentages are by weight, unless stated otherwise, and temperatures are in degrees Celsius.

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Examples

In the following Examples, the base fuel was a Swedish Class I Diesel Fuel. The properties of said base fuel are highlighted in Table 1.

5

TABLE 1

Density @ 15°C (IP365/ASTM D4052) g/cm ³	0.8150
Distillation (IP123/ASTM D86)	
IBP °C	186.0
10%	207.0
20%	214.0
30%	222.0
40%	229.0
50%	235.0
60%	242.0
70%	248.0
80%	256.0
90%	264.0
95%	272.0
FBP	290.5
Cetane Number ASTM D613	54.5
V.K. @ 40°C (IP71/ASTM D445) cSt	2.030
Sulphur WDXRF (ASTM D2622) mg/kg	<5
Cloud Point (IP219) °C	-32
CFPP (IP309) °C	-37
HPLC Aromatics (IP391 Mod)	
Mono %m	4.4
Di %m	<0.1
Tri %m	<0.1

Standard methods in the art were employed for determining smoke value, opacity, particulate content, NO emissions and CO emissions.

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1,1,3-Trimethoxypropane (TMOP) and 1,1,3-triethoxypropane (TEOP) may be prepared in accordance with the method described in FR-A-1447138.

Example 1

Results of Bench Engine Emission Tests with diesel fuel blended with 1,1,3-Trimethoxypropane.

Blends of TMOP with a Swedish Class I diesel fuel were tested in a bench engine. The engine was a single cylinder diesel research engine manufactured by AVL/LEF based on a Volvo D12 unit. The fuel injection system employed ECU controlled unit injection. An intake boost compressor was fitted and the tests were done with an intake manifold pressure of 140kPa absolute. The speed was 1200rpm and the torque was maintained constant (130Nm) for all tests and was approximately half full load (rated for hydrocarbon fuel).

The results in Table 2 show that TMOP reduces the smoke emissions. For TMOP compositions of 57.8% wt. and greater, the smoke measurements (in units of Filtered Smoke Number (FSN)) were indistinguishable from zero within experimental uncertainty. Such low levels of smoke emission are first achieved at about 50 % wt. TMOP. CO emissions are also very strongly reduced. The small increase in NOx emissions is offset by the large reduction in particulate matter.

The detailed results are of course dependent on the nature of the base fuel and the engine running conditions, but the qualitative behaviour is always the same: the soot emissions drop to essentially zero when a major proportion of the fuel is TMOP, as indicated by the smoke measurements (see Figure).

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TABLE 2

TMOP % wt.	Smoke, FSN	NO, g/kW.h	CO, g/kW.h
0.0%	1.28	7.96	3.14
23.1%	0.35	8.19	1.61
34.7%	0.10	8.50	0.91
46.2%	0.05	8.77	0.61
57.8%	0.01	9.09	0.44
69.3%	0.00	9.50	0.33
92.5%	0.00	10.28	0.22

Example 2

5 A further test in the same engine under the same load/speed/boost conditions and with the same base fuel as in Example 1 showed that particulate emissions are reduced by more than an order of magnitude with 57.8 % wt. (50 % v.) TMOP (see Table 3).

TABLE 3

	Smoke FSN	Opacity %	Particulate g/kW.h	NO g/kW.h	CO g/kW.h
Base fuel	1.21	4.9	0.219	8.28	2.86
Base fuel (repeat measurement)	1.32	4.78	0.25	8.11	3.36
Base fuel + 57.8 % wt. TMOP	0.01	0.47	0.018	9.3	0.29

Example 3

15 A further test in the same engine under the same load/speed/boost conditions and with the same base fuel as in Example 1 showed that particulate emissions are reduced by more than an order of magnitude with 73 % wt. TEOP (see Table 4).

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TABLE 4

	Smoke FSN	Opacity %	NOx g/kW.h	CO g/kW.h
Base Fuel	1.16	5.12	9.03	3.00
Base Fuel (repeat measurement)	1.17	4.94	9.04	3.17
Base Fuel + 73 % wt. TEOP	0.03	0.13	9.13	0.41

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TS7569CLAIMS

1. A fuel composition for a compression-ignition engine comprising one or more trialkoxyalkanes, wherein said one or more trialkoxyalkanes are present in an amount in the range of from 50 to 100 % wt. based on said fuel composition.
2. A fuel composition according to claim 1, wherein said one or more trialkoxyalkanes are present in an amount in the range of from 55 to 100 % wt. based on said fuel composition.
3. A fuel composition according to claim 2, wherein said one or more trialkoxyalkanes are present in an amount in the range of from 57 to 100 % wt. based on said fuel composition.
4. A fuel composition according to claim 3, wherein said one or more trialkoxyalkanes are present in an amount in the range of from 57 to 75 % wt. based on said fuel composition.
5. A fuel composition according to any one of Claims 1 to 4, wherein said one or more trialkoxyalkanes are present in an amount sufficient to reduce smoke emissions of the fuel composition to zero upon combustion.
6. A fuel composition according to any one of Claims 1 to 5, wherein said one or more trialkoxyalkanes are selected from 1,1,3-trimethoxypropane and 1,1,3-triethoxypropane.
7. A method of operating a compression-ignition engine, which comprises introducing into the combustion chambers of said engine a fuel composition according to any one of Claims 1 to 6.

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8. The use in a compression-ignition engine of a fuel composition according to any one of Claims 1 to 6.
9. The use in a compression-ignition engine of a fuel composition according to any one of Claims 1 to 6, to reduce the levels of soot produced in said engine as compared to the levels of soot produced when the engine is operated using a fuel composition not comprising said one or more trialkoxyalkanes.

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INVESTOR IN PEOPLE

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 Claims searched: 1-9

Examiner: Darren Handley
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Patents Act 1977 Search Report under Section 17

Databases searched:

UK Patent Office collections, including GB, EP, WO & US patent specifications, in:

UK Cl (Ed.T): C5G (GAA, GAB)

Int Cl (Ed.7): C10L 1/02, 1/18

Other: Online: WPI, EPODOC, JAPIO

Documents considered to be relevant:

Category	Identity of document and relevant passage	Relevant to claims
Y	WO 98/56879 A1 (ELF) - see claims 2 and 3.	6
A	US 5308365 A (KESLING) - see column 3, line 54- column 4, line 42.	
X, Y	US 5268008 A (KANNE) - see column 2, line 13- column 3, line 45.	X: 1-5, 7-9 Y: 6
X, Y	US 4647288 A (DILLON) - see column 2, line 13- column 3, line 66.	X: 1-5, 7-9 Y: 6

X	Document indicating lack of novelty or inventive step	A	Document indicating technological background and/or state of the art.
Y	Document indicating lack of inventive step if combined with one or more other documents of same category.	P	Document published on or after the declared priority date but before the filing date of this invention.
&	Member of the same patent family	E	Patent document published on or after, but with priority date earlier than, the filing date of this application.

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